[illegible] IN CUBIC AND [illegible] C [illegible] ALS

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Thesis submitted to the Indian Institute of Technology,
Delhi, in partial fulfilment for the Degree of
Doctor of Philosophy
1973

ACKNOWLEDGEMENTS

The author wishes to express his deep sense of gratitude to esteemed guide and supervisor, Dr.R.G.Men ratta, for his invaluable help, kind encouragement and constructive suggestions at various stages, without which the present work would not have been completed. The author is indebted to his colleagues Dr.Raj Kamal, now at Punjabi University,Pati la, Mr. R.G.Gupta, Miss Kusma Agarwal and Mr. O.P.Malik for various discussions during the progress of the work.

The cooperation, help, and interest rendered by Dr.P.K.C.Pillai should also be gratefully acknowledged. The interest shown by Prof.K.L.Chopra and Prof.M.S.Sodha are also acknowledged. Further, the author will not forget invaluable help rendered by Mr.K.V.Reddy in taking the electron paramagnetic resonance spectra and X-ray powder photographs at Solid State Physics Laboratories, Delhi. The author likes to express his sincere thanks to the 'Chemical Physics' group at Tata Institute of Fundamental Research for their help in determining the magnetic susceptibility.

The author is greatly indebted to his parents Smt. S.Vijaya Lakshmi and Sri S.Venkata Rao for their many sacrifices and love, without which the author would not have had the basic education in Physics.

Besides, in this academic achievement there were many personalities whose keen interest and inspiration

provided a favourable atmosphere to work. I should lik to specifically mention the names of Mr. S.Pradhaman, Dr. T.Hymavathi, Mr. S.Chandrasekhar and Mr. S.V.Sastri.

The help of many other colleagues in the Department is also acknowledged. The help rendered by Mr. S.V.Narayana Rao during the preparation of the manuscript should not go unacknowledged.

The thesis could not have been completed but for painstaking and accurate typing by Mr. T.N.Gupta.

The author wishes to acknowledge the financial assistance provided by the Director, I.I.T. Delhi and the C.S.I.R., India.

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CHAPTER P

llowing Mossbauer's discovery[1,2] of recoilless gamma-ray emission and absorption, it became clear that this effect - commonly referred to as the "Mossbauer effect" - would be germane to a very broad spectrum of physical and chemical investigations. Many of the chemical and solid state applications of the Mössbauer effect[3-6] depend on the fact that the available gamma-ray line widths are small compared to the characteristic energy of interaction of nuclei with their surrounding electrons. Befor Mossbauer's discovery, the possibility of being able to resolve the nuclear hyperfine structure by observing the gamma-ray betwee nuclear levels had been universally discounted, although some indirect measurement like γ-γ correlation experiments and nuclear aligment experiments did give some marginal insight into the nuclear hyperfine structure. It is the influence of the chemical environment on the emission and absorption of γ-radiation that constitutes the basis of applications of the Mossbauer effect to chemical investigations.

Following this discovery, the possibilities for studying the influence of the crystal structure and of the electronic shells of atoms on nuclear transformations (in particular, on the energy of γ-quanta) has come into perspective. The phenomenon is characterized by an unusually high resolving abilit The Mossbauer effect manifests itself quite distinctly against a background of other nonresonance processes of absorption and scattering of γ-quanta in solid bodies. The room temperature EPR studies of Fe^{2+} ion in solids are not possible due to the shortening of electronic relaxation times by lattice defects. To get a direct information about the covalency and bonding of Fe^{2+} ions in solids at RT the Mossbauer Effect is the only tool available. A detail account of the relative merits and demerits of the Mossbauer Effect (ME) over the optical absorption, EPR and other conventional methods is given in chapter I (I.3).

Although a lot of theoretical and experimental work has been done on the study of quadrupole-interactions in solids by Mossbauer spectroscopy, there are areas which need further consideration. Present thesis is an attempt to exploit two such areas (i) to investigate the imperfections and quadrupole interactions in Co^{57} diffused single crystals of KBr (cubic symmetry) and, (ii) to study the crystal field and covalency effects on nuclear quadrupole interaction in a transition metal ion complex Fe (NH$_4$SO$_4$)$_2$6H$_2$O (known as Tutton salt) diluted with Cu^{2+} ions and Ni^{2+} ions separately. The study of iron group elements doped in alkali halides have been the subject of considerable interest mostly after the work of Watkins[12]. In recent years, the impurities in alkali halide crystals have been found to have a profound influence on the coloration processes in alkali halides in general and the interest has rapidly grown in such studies partly because of their importance in understanding the optical and electronic processes in solids and partly because of many practical applications of impurity doped alkali halides, e.g., in radiation dosimeters, dark trace screens etc. when doubly or triply charged ionozined impurity is doped in a alkali halide crystal, the number of cation vacancies is enhanced in the crystal due to the mechanism of charge compensation. Several interesting observations of quadrupole interactions have been observed. From the observed Moss ber ectrum of Co^{57} doped single crystals, the charge conversion of the impurity ions and the change in the lattice symmetry around the impurity ion are discussed on the basis of proposed models.

Ferrous ammonium sulphate hexahydrate (FAS) is a ve stable ionic compound and the high spin Fe^{2+} ion exhibit very interesting results due to covalency and crystal field effects^{13} Although, susceptibility^{14,15} PMR^{16} and optical studies^{17} have been made on FAS, a basic understanding of 3d electron distribution at the Fe^{2+} ion is missing. The present study of F diluted with Cu^{2+} ion is undertaken with the hope that t information obtained from the results of quadrupole interaction would be of great help to develope a more realistic model to explain better all the experimental results. A very interesting variation of the quadrupole splitting with concentration of para magnetic impurities like Cu^{2+} and Ni^{2+} is observed and a attemp to explain the results both qualitatively and quantitatively is made.

For Mossbauer effect measurements a simple cam driv mechanical drive operatable in a constant velocity mode is used. The Mossbauer source is mounted on this drive and the sodium iodide crystal is used to detect the γ -rays transmitted throu the absorber. The observed spectra are repeated on another spectrometer which consists of an electromagnetic type drive eratable in a constant acceleration mode and used in conjuncti with a multichannel analyser.

Theoretical models are proposed to explain the variation of quadrupole splitting. As a consequence, an analysis is reported to estimate the covalent bond energies between a few 3d metal ions. The covalency effects on ferrous tutton salts and the correlation with optical measurements is clearly brought out.

Though the summary, evaluation and recommendations based on this work are given at the end of this thesis, the important conclusions of this work are as follows. When iron is doped in KBr single crystal, ferric iron goes to an interstial site, a conclusion which does not immediately follow from other studies. When an divalent impurity like Cu^{2+} ion is doped in FAS, the Fe^{2+} ion takes up two nonequivalent sites as far as EFG is concerned. The quadrupole splitting shows an interesting variation with the concentration of the doped Cu^{2+} ions. This variation is used to calculate the hetronuclear bond energy between transition metal ions, a parameter of immense importance in the understanding of chemical structure.

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